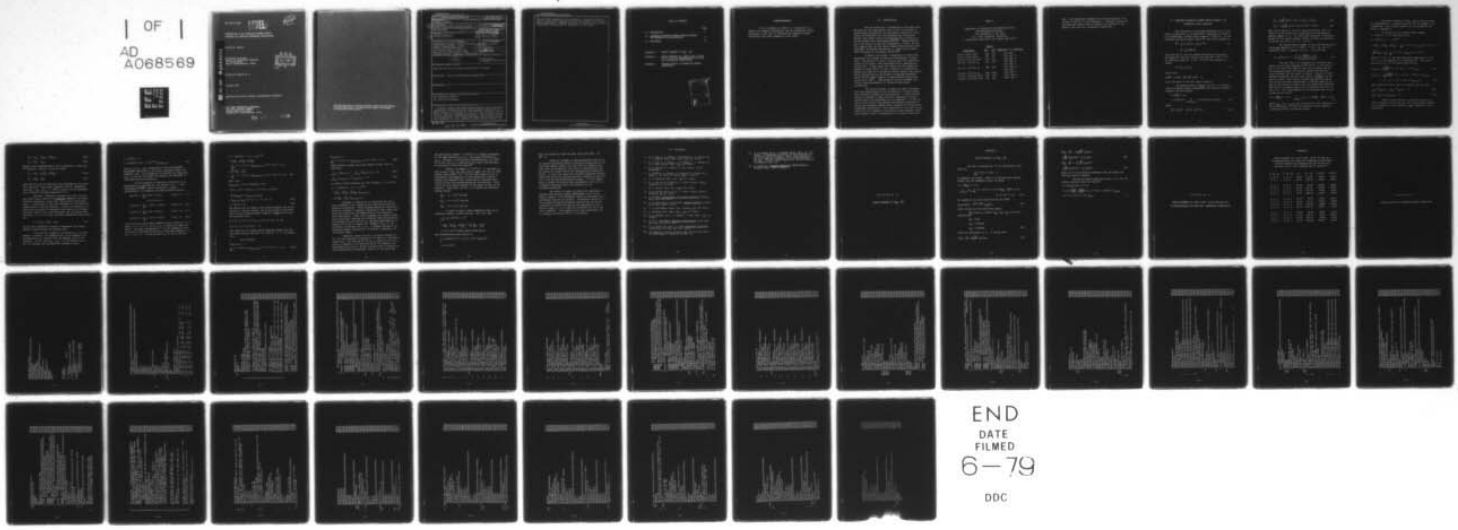
AD-A068 569 LOWELL UNIV RESEARCH FOUNDATION MASS F/G 20/10
COMPUTATION OF H20 QUADRUPOLE MOMENT MATRIX ELEMENTS FOR PRESSU--ETC(U)
JAN 79 R W DAVIES F19628-77-C-0053
UNCLASSIFIED ULRF-400/CAR AFGL-TR-79-0035 NL

| OF |
AD
A068569



END
DATE
FILMED
6-79
DDC

AFGL-TR-79-0035

LEVEL II

# COMPUTATION OF $H_2O$ QUADRUPOLE MOMENT MATRIX ELEMENTS FOR PRESSURE BROADENING CALCULATIONS

Richard W. Davies

University of Lowell
Center for Atmospheric Research
450 Aiken Street
Lowell, Massachusetts 01854





Scientific Report No. 2

January 1979



AIR FORCE GEOPHYSICS LABORATORY
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
HANSCOM AFB, MASSACHUSETTS 01731

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

| REPORT DOCUMENTATION PAGE | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|---|
| 1. REPORT NUMBER: AFGL-TR-79-0035 | 2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle): COMPUTATION OF $H_2O$ QUADRUPOLE MOMENT MATRIX ELEMENTS FOR PRESSURE BROADENING CALCULATIONS | 5. TYPE OF REPORT & PERIOD COVERED: Scientific Report No. 2 |
| | 6. PERFORMING ORG. REPORT NUMBER: ULRF-400/CAR |
| 7. AUTHOR(s): Richard W. Davies | 8. CONTRACT OR GRANT NUMBER(s): F19628-77-C-0053 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS: University of Lowell, Center for Atmospheric Research, 450 Aiken Street, Lowell, Massachusetts 01854 | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 61102F; 2310G1AF |
| 11. CONTROLLING OFFICE NAME AND ADDRESS: Air Force Geophysics Laboratory, Hanscom AFB, Massachusetts 01731, Contract Monitor: Francis X. Kneizys/OPI | 12. REPORT DATE: January 1979 |
| | 13. NUMBER OF PAGES: 52 |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): 49p. | 15. SECURITY CLASS. (of this report): Unclassified |
| | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

$H_2O$ Quadrupole Moments

$H_2O$ Pressure Broadening

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Recent tunable laser measurements indicate that theoretical linewidths, calculated for $H_2O$ self-broadened transitions and based solely on the effects of dipole-dipole collisions, are too small at high and intermediate J values. This suggests neglect of other important scattering mechanisms, such as dipole-quadrupole interactions. This report discusses computational procedures necessary to obtain quadrupole moment matrix elements for

DD FORM 1 JAN 73 1473

409 596

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

$H_2^{\uparrow}O$ and other asymmetric rotor molecules. Computer programs to obtain these matrix elements have been constructed and are presently operational. Numerical results for some low J quadrupole transitions are presented in Appendix B of the report.

TABLE OF CONTENTS


| | | Page |
|---|---|---|
| 1.0 | INTRODUCTION | 1 |
| 2.0 | PERMANENT QUADRUPOLE MOMENT MATRIX ELEMENTS FOR ASYMMETRIC ROTOR MOLECULES | 4 |
| 3.0 | REFERENCES | 13 |

APPENDIX A — MATRIX ELEMENTS OF $[\Phi^2_{z\alpha} - \frac{1}{3}]$

APPENDIX B — MATRIX ELEMENTS OF A AND B (EQS. 18-20) FOR $H_2O$ IN A IR REPRESENTATION FOR SOME LOW $J^2$ QUADRUPOLE TRANSITIONS.

APPENDIX C — PROGRAM LISTING OF QUADRUPOLE MOMENT SUBROUTINES


## ACKNOWLEDGEMENTS

It is a pleasure to thank S. A. Clough and F. X. Kneizys for numerous discussions, and for substantial active assistance in the task of combining our quadrupole moment subroutines with their asymmetric rotor codes.

# 1.0 INTRODUCTION

The work which will be presented in this report was motivated by our observations that, if only the effects of dipole-dipole interactions are considered, theoretical calculations of halfwidths for self-broadened $H_2O$ transitions exhibit some rather serious discrepancies with recently reported tunable laser measurements.[1,2,3,4] These discrepancies occur mainly at high and intermediate J values, and obtain using either the well-known Anderson-Tsao-Curnutte (ATC) theory[5,6] of pressure broadening, or a more recent method (QFT) developed by the present author.[7,8]

In Table I we present a comparison of theory with experiment for a number of high and intermediate J transitions. The results in Table I indicate that the theoretical widths are too small, with percentage errors sometimes exceeding 50%. In most cases the results are only weakly dependent on which theory is used. However, all theoretical numbers are based on a calculation which includes only dipole-dipole interactions as the dominant scattering mechanism. These results suggest neglect of some important scattering mechanism at high J. Some possibilities are exchange scattering, dipole-quadrupole, or dipole-induced-dipole interactions.

Our initial efforts to remove the above discrepancies have concentrated on the contribution of dipole-quadrupole collisions between the $H_2O$ molecules. A future journal article is planned in which detailed comparison of the expanded theory with experiment will be presented. In this report we will outline the computational methods necessary to obtain $H_2O$ quadrupole moment matrix elements for the pressure-broadening calculations. This computation is far from trivial since $H_2O$ is an asymmetric top molecule whose permanent quadrupole moment cannot be represented by a single scalar quan-

TABLE I

Comparison of Theoretical and Experimental $H_2O$
Self-Broadened Halfwidths
(All halfwidths in $cm^{-1}/atm$;
rot = pure rotational transition;
† measurement near 382°K, all others near 297°K)

| | Theory | | |
|---|---|---|---|
| Transition | ATC | QFT | Experiment and Reference |
| 8,1,8 → 9,4,5 (rot) | .409 | .402 | .559, Ref. 3 |
| 8,3,6 → 9,6,3 (rot) | .343 | .377 | .611, Ref. 3 |
| 11,1,10 → 12,4,9 (rot) | .261 | .257 | .319, Ref. 3 |
| 12,2,11 → 13,1,12 $\nu_2$ | .160 | .140 | .228, Ref. 2 |
| | | | .170, Ref. 4 |
| 15,1,15 → 16,0,16 $\nu_2$ | .098 | .083 | .177, Refs. 1, 2 |
| | | | .166, Ref. 4 |
| 15,2,14 → 16,1,15 $\nu_2$ | .084 | .085 | .203, Ref. 2 |
| 17,0,17 → 18,3,16 (rot) | .085 | .078 | .125†, Ref. 3 |
| 19,0,19 → 20,3,18 (rot) | .063 | .063 | .089†, Ref. 3 |

tity. The theoretical framework for the calculations is developed in Section 2.0 and Appendix A. Numerical results for $H_2O$ quadrupole moment matrix elements are presented in Appendix B for some low J quadrupole transitions.

## 2.0 PERMANENT QUADRUPOLE MOMENT MATRIX ELEMENTS FOR ASYMMETRIC ROTOR MOLECULES

The calculation of pressure broadening due to quadrupole interactions can be expressed[7] completely in terms of an m-independent, reduced matrix element, $\langle J||Q^t||J'\rangle$, of the traceless quadrupole moment tensor $\overleftrightarrow{Q}^t$, the latter defined as

$$\overleftrightarrow{Q}^t = \sum_i e_i \left[\vec{r}_i \vec{r}_i - \frac{1}{3} r_i^2 \overleftrightarrow{I}\right], \tag{1}$$

$$= \overleftrightarrow{Q} - \frac{1}{3} \mathrm{Tr}(\overleftrightarrow{Q})\, \overleftrightarrow{I}, \tag{2}$$

where the sum is over all charged particles in the molecule, and where $\overleftrightarrow{I}$ is the unit tensor, such that $\overleftrightarrow{I}\cdot\vec{A} = \vec{A}\cdot\overleftrightarrow{I} = \vec{A}$ for an arbitrary vector $\vec{A}$. In Eq. (2), $\overleftrightarrow{Q}$ is the quadrupole moment tensor

$$\overleftrightarrow{Q} = \sum_i e_i \vec{r}_i \vec{r}_i, \tag{3}$$

and we note

$$\mathrm{Tr}(\overleftrightarrow{Q}^t) = \mathrm{Tr}(\overleftrightarrow{Q}) - \frac{1}{3} \mathrm{Tr}(\overleftrightarrow{Q})\, \mathrm{Tr}(\overleftrightarrow{I}) = 0, \tag{4}$$

since the trace of the unit tensor equals 3.

The reduced matrix element $\langle J||Q^t||J'\rangle$ is defined using the Wigner-Eckhart theorem[9,10] for traceless symmetric tensors, via the equation

$$\langle J\ m|\overleftrightarrow{Q}^t|J'\ m'\rangle$$

$$= \langle J||Q^t||J'\rangle \sum_{M=0,\pm1,\pm2} (J'2\text{-}m'\text{-}M|J'2\ J\text{-}m)\, \overleftrightarrow{T}_M, \tag{5}$$

where

$$\overleftrightarrow{T}_0 = \frac{2}{3}\left[\hat{Z}\hat{Z} - \frac{1}{2}\hat{X}\hat{X} - \frac{1}{2}\hat{Y}\hat{Y}\right], \tag{5a}$$

$$\overleftrightarrow{T}_{\pm 2} = \frac{1}{2}\sqrt{\frac{2}{3}}\,[(\hat{X}\,\hat{X} - \hat{Y}\,\hat{Y}) \mp i(\hat{X}\,\hat{Y} + \hat{Y}\,\hat{X})], \tag{5b}$$

$$\overleftrightarrow{T}_{\pm 1} = \mp\frac{1}{2}\sqrt{\frac{2}{3}}\,[(\hat{Z}\,\hat{X} + \hat{X}\,\hat{Z}) \mp i(\hat{Z}\,\hat{Y} + \hat{Y}\,\hat{Z})]. \tag{5c}$$

Here (X,Y,Z) refer to a set of spaced-fixed axes, and Z is taken to be the direction of quantization for the magnetic quantum numbers m, m'. For non-linear molecules $|J\rangle$ actually stands for all quantum numbers (except m) which are necessary to specify the state, i.e. $|J\rangle = |J\tau\cdot\cdot\rangle$.

The reduced matrix element is then obtained by calculating <u>any</u> component of $\langle J\ \tau\ m|\overleftrightarrow{Q}^t|J'\ \tau'\ m'\rangle$, e.g. the $\hat{Z}\,\hat{Z}$ component, which is diagonal in m, m'. Thus, we have

$$\langle J\ \tau||Q^t||J'\ \tau'\rangle = \frac{3}{2}\,\frac{\langle J\ \tau\ m|\overleftrightarrow{Q}^t_{ZZ}|J'\ \tau'\ m\rangle}{(J'2\text{-}m\ 0|J'2\ J\text{-}m)}\,. \tag{6}$$

The next step is to transform to a principal axis system (x,y,z) which diagonalizes $\overleftrightarrow{Q}^t$ and $\overleftrightarrow{Q}$. In the case of $H_2O$, it is clear from symmetry that the principal axes for the quadrupole moment and inertial tensors are identical except possibly for the choice of origin. However, in most pressure-broadening theories this choice is <u>fixed</u> to be the center of mass. This results because one typically writes the various multipole interactions as $V(\vec{R}_i\text{-}\vec{R}_j)$ where $\vec{R}_i$, $\vec{R}_j$ specify the centers of mass of the two interacting molecules. This point is somewhat subtle and is discussed more fully in Ref. (17). The transformation to the principal axis (x,y,z) system can be written

$$\langle J\ \tau\ m|\overleftrightarrow{Q}^t_{ZZ}|J'\ \tau'\ m\rangle = \sum_{\alpha=x,y,z} Q_{\alpha\alpha}\,\langle J\ \tau\ m|[\Phi^2_{Z\alpha} - \tfrac{1}{3}]|J'\ \tau'\ m\rangle, \tag{7}$$

where $Q_{\alpha\alpha} = \sum_i e_i\, r_{i\alpha}\, r_{i\alpha}$ are the principal axis components of $\overleftrightarrow{Q}$, and where $\Phi_{Z\alpha} = \hat{Z}\cdot\hat{\alpha}$ are the direction cosine operators connecting the two coordinate systems.

The matrix elements of $[\Phi^2_{Z\alpha} - \frac{1}{3}]$ can be evaluated by transforming to a representation $|J\ K\ m\rangle$ of symmetric top eigenstates. Some further details of this evaluation are given in Appendix A.

The result for the reduced matrix element $\langle J\ \tau||Q^t||J'\ \tau'\rangle$ is then found to be

$$\langle J\ \tau||Q^t||J'\ \tau'\rangle = (-1)^{J+J'}$$

$$\cdot \{(Q_{zz} - \tfrac{1}{2} Q_{xx} - \tfrac{1}{2} Q_{yy}) \cdot \sum_{KK'} \langle J\ \tau|J\ K\rangle A_{JK;J'K'} \langle J'\ K'|J'\ \tau'\rangle$$

$$- \sqrt{\tfrac{3}{4}} (Q_{xx} - Q_{yy}) \sum_{KK'} \langle J\ \tau|J\ K\rangle B_{JK;J'K'} \langle J'\ K'|J'\ \tau$$

where $\langle J'\ K'|J'\ \tau'\rangle$ are the eigenvector components of state $|J'\ \tau'\rangle$ in the symmetric top representation. The A and B matrices in Eq. (7) are given explicitly by

$$A_{JK;J'K'} = \sqrt{\frac{2J'+1}{2J+1}} (J'\ 2\ K'\ 0|J'\ 2\ J\ K')\ \delta_{K,K'}, \tag{9a}$$

$$B_{JK;J'K'} = \frac{1}{\sqrt{2}} \sqrt{\frac{2J'+1}{2J+1}} \{(J'\ 2\ K'\ 2|J'\ 2\ J(K'+2))\ \delta_{K,K'+2}$$

$$+ (J'\ 2\ K' - 2|J'\ 2\ J(K'-2))\ \delta_{K,K'-2}\}, \tag{9b}$$

and it may be verified that A, B satisfy the sum rules

$$\sum_{J'K'} A^2_{JK;J'K'} = \sum_{J'K'} B^2_{JK;J'K'} = 1, \tag{10a}$$

$$\sum_{J'K'} A_{JK;J'K'}\ B_{JK;J'K'} = 0. \tag{10b}$$

Several points should be noted before going on. First, from Eq. (8) we note that the reduced matrix element for an asymmetric rotor depends on <u>two</u> independent scalar parameters

$$Q_1 = (Q_{zz} - \tfrac{1}{2} Q_{xx} - \tfrac{1}{2} Q_{yy}), \tag{11a}$$

$$Q_2 = (Q_{xx} - Q_{yy}). \tag{11b}$$

However, this parameterization can be expressed in other useful fashions. From Eq. (2) we note that

$$Q_1 = (Q^t_{zz} - \tfrac{1}{2} Q^t_{xx} - \tfrac{1}{2} Q^t_{yy}), \tag{12a}$$

$$Q_2 = (Q^t_{xx} - Q^t_{yy}), \tag{12b}$$

where the $Q^t$'s are the principal axis components of the traceless tensor $\overleftrightarrow{Q}^t$. These three components are not independent since $Q^t_{xx} + Q^t_{yy} + Q^t_{zz} = 0$. Hence $Q_1$ and $Q_2$ can be parameterized in terms of any <u>two</u> components of $Q^t$.

Secondly, it should be pointed out in Eq. (8) that the labels (x,y,z) refer to an <u>arbitrary</u> symmetric top representation (arbitrary, except that (x,y,z) must be principal axes). In particular, z need not correspond to the (two-fold) symmetry axis of the $H_2O$ molecule. In fact the numerical results which we present in Appendix B are based on a IR representation, where (z,x,y) are associated with the lowest-order constants, A > B > C, in the rotational-vibrational Hamiltonian via

$$H = B J_x^2 + C J_y^2 + A J_z^2. \tag{13}$$

For $H_2O$ the intermediate constant B represents the inverse moment of inertia about the symmetry axis.

Of course for a symmetric top molecule, it is most natural to choose z, the symmetry axis of the symmetric top representation, to coincide with the symmetry axis of the molecule. In this case $(Q_{xx} - Q_{yy}) = 0$, the second term in Eq. (8) vanishes, and the equation collapses to give

$$\langle J\ \tau||Q^t||J'\ \tau'\rangle$$

$$= \langle J\ K||Q^t||J'\ K'\rangle = (-1)^{J'+J}\ Q_1\ A_{JK;J'K'}, \qquad (14)$$

where $Q_1 = (Q_{zz} - Q_{xx})$ corresponds to the Buckingham[11], Birnbaum[12] definition of the scalar quadrupole moment for symmetric tops. This definition is one-half the value used, e.g., by Tsao and Curnutte[6] and Benedict and Kaplan[13] in discussing pressure-broadening.

For the purposes of numerical computation it is advantageous to transform Eq. (8) further using the Wang transformation[14,15], which corresponds to forming combinations of the symmetric top wave functions according

$$|E_+(J\ K)\rangle = \frac{1}{\sqrt{2}}\{|J\ K\rangle + |J\text{-}K\rangle\} \qquad K \text{ even} > 0, \quad (15a)$$

$$= |J\ 0\rangle\ (K = 0)$$

$$|E_-(J\ K)\rangle = \frac{1}{\sqrt{2}}\{-|J\ K\rangle + |J\text{-}K\rangle\} \qquad K \text{ even} > 0, \quad (15b)$$

$$|O_+(J\ K)\rangle = \frac{1}{\sqrt{2}}\{|J\ K\rangle + |J\text{-}K\rangle\} \qquad K \text{ odd} > 0, \quad (15c)$$

$$|O_-(J\ K)\rangle = \frac{1}{\sqrt{2}}\{-|J\ K\rangle + |J\text{-}K\rangle\} \qquad K \text{ odd} > 0. \quad (15d)$$

Let us write the above Wang (symmetric top) states as $|J\ K\ \nu\rangle$ where $\nu = 1, 2, 3, 4 = E_+, E_-, O_+, O_-$ denotes the Wang symmetry. The exact eigenstates $|J\ \tau\rangle$ of the asymmetric rotor can also be classified according to their Wang symmetry, i.e. $|J\ \tau\rangle = |J\ \tau\ \nu\rangle$. In this notation Eq. (8) can be written

$$\langle J\ \tau\ \nu||Q^t||J'\ \tau'\ \nu'\rangle = (-1)^{J'+J}$$

$$\cdot \{(Q^t_{zz} - \tfrac{1}{2} Q^t_{xx} - \tfrac{1}{2} Q^t_{yy})$$

$$\cdot \sum_{K,K'} \langle J\ \tau\ \nu|J\ K\ \nu\rangle A_{JK\nu;J'K'\nu'} \langle J'\ K'\ \nu'|J'\ \tau'\ \nu'\rangle$$

$$-\sqrt{\tfrac{3}{4}} (Q^t_{xx} - Q^t_{yy})$$

$$\cdot \sum_{KK'} \langle J\ \tau\ \nu|J\ K\ \nu\rangle B_{JK\nu;J'K'\nu'} \langle J'\ K'\ \nu'|J'\ \tau'\ \nu'\rangle\}. \quad (16)$$

Here, e.g.,

$$A_{JK4;J'K'4} = \langle O_-(J\ K)|A|O_-(J'\ K')\rangle$$

$$= \tfrac{1}{2} (-\langle J\ K| + \langle J\text{-}K|)\ A\ (-|J'\ K'\rangle + |J'\text{-}K'\rangle)$$

$$= \tfrac{1}{2} \{A_{JK;J'K} + A_{J-K;J'-K}\}\ \delta_{K,K'}$$

$$= A_{JK;J'K}\ \delta_{K,K'} \text{ for } \Delta J = J - J' = 0, \pm 2 \quad (17a)$$

$$= 0 \text{ for } \Delta J = \pm 1. \quad (17b)$$

The results for all other A and B matrix elements can be obtained in a similar fashion, and it may readily be verified that the non-vanishing matrix elements of <u>both</u> A and B obey the selection rules

$$E_+ \nrightarrow E_+,\ E_- \nrightarrow E_-,\ O_+ \nrightarrow O_+,\ O_- \nrightarrow O_- \text{ for } \Delta J = 0, \pm 2,$$

$$E_+ \nrightarrow E_-,\ O_+ \nrightarrow O_- \text{ for } \Delta J = \pm 1.$$

That there are no allowed matrix elements between even and odd states follows from Eqs. (9) since $\Delta K = K - K'$ is always even.

We now define

$$A_{J\tau\nu;J'\tau'\nu'} =$$

$$\sum_{KK'} \langle J\ \tau\ \nu|J\ K\ \nu\rangle A_{JK\nu;J'K'\nu'} \langle J'\ K'\ \nu'|J'\ \tau'\ \nu'\rangle, \quad (18a)$$

$$B_{J\tau\nu;J'\tau'\nu'} =$$

$$\sum_{KK'} \langle J\ \tau\ \nu | J\ K\ \nu\rangle\ B_{JK\nu;J'K'\nu'}\ \langle J'\ K'\ \nu' | J'\ \tau'\ \nu'\rangle. \qquad (18b)$$

These matrices satisfy sum rules similar to Eqs. (10), in particular

$$\sum_{J'\tau'\nu'} A^2_{J\tau\nu;J'\tau'\nu'} = \sum_{J'\tau'\nu'} B^2_{J\tau\nu;J'\tau'\nu'} = 1, \qquad (19a)$$

$$\sum_{J'\tau'\nu'} A_{J\tau\nu;J'\tau'\nu'}\ B_{J\tau\nu;J'\tau'\nu'} = 0. \qquad (19b)$$

In terms of these matrices, Eq. (16) assumes its final form

$$\langle J\ \tau\ \nu || Q^t || J'\ \tau'\ \nu'\rangle = (-1)^{J+J'}$$

$$\cdot \{(Q^t_{zz} - \tfrac{1}{2} Q^t_{xx} - \tfrac{1}{2} Q^t_{yy})\ A_{J\tau\nu;J'\tau'\nu'}$$

$$- \tfrac{3}{4} (Q^t_{xx} - Q^t_{yy})\ B_{J\tau\nu;J'\tau'\nu'}\}. \qquad (20)$$

Programs to compute the A, B matrices for $H_2O$ and other asymmetric rotor molecules have been written and are presently operational. These programs operate as subroutines which are attached to programs, developed at AFGL, which generate the eigenvalues and eigenvectors of the asymmetric rotor Hamiltonian. These latter programs also include vibrational-rotational coupling via the Watson Hamiltonian method. The programs are quite efficient, requiring approximately 60 seconds of CP time to compute the strongest ($\Delta K_a = 0, \pm 2$) quadrupole transitions for $J \leq 22$. A program listing of our quadrupole moment subroutines is furnished in Appendix C of the present report.

Numerical results for the A, B matrix elements in Eq. (20) are presented in Appendix B for some low J quadrupole transitions. The labeling of the $K_a$, $K_c$ states in the tabulation of Appendix B is consistent with a IR symmetric top representation for $H_2O$. We have verified that our methods do give representation-independent results, in the sense that

the same matrix element $\langle J\ \tau||Q^t||J'\ \tau'\rangle$ always corresponds to the same energies $E_{J\tau}$, $E_{J'\tau'}$ and energy difference $E_{J\tau} - E_{J'\tau'}$. However, if one switches representations, e.g. from IR to IIR, the $K_a$, $K_c$ labeling of the states also switches, as discussed in Allen and Cross.[16]

Finally, to compute $\langle J\ \tau||Q^t||J'\ \tau'\rangle$, one needs to know values of $Q^t_{xx}$, $Q^t_{yy}$, $Q^t_{zz}$ (which, again, are not all independent since $Tr(Q^t) = 0$). For $H_2O$ there appears to be no experimental determination of these quantities, however, Stogryn and Stogryn[17] have listed fairly consistent theoretical values from quantum mechanical calculations. Their values are also quoted relative to the center of mass of the molecule. From Table 3 of Ref. 17 we deduce the following average values:

$$Q^t_{xx} = .12 \times 10^{-26} \text{ esu-cm}^2$$

$$Q^t_{yy} = -.72 \times 10^{-26} \text{ esu-cm}^2$$

$$Q^t_{zz} = .60 \times 10^{-26} \text{ esu-cm}^2$$

In order to make a simple comparison with the $N_2$ quadrupole moment, we note from Eqs. (19), (20) that

$$\sum_{J'\tau'} |\langle J\ \tau||Q^t||J'\ \tau'\rangle|^2$$

$$= (Q^t_{zz} - \tfrac{1}{2} Q^t_{xx} - \tfrac{1}{2} Q^t_{yy})^2 + \tfrac{3}{4} (Q^t_{xx} - Q^t_{yy})^2$$

$$= 1.34 \times 10^{-52} \text{ (from values listed above).}$$

The corresponding result for $N_2$ is

$$\sum_{J'} |\langle J||Q^t||J'\rangle|^2 = (1.52 \times 10^{-26} \text{ esu-cm}^2)^2$$

$$= 2.31 \times 10^{-52},$$

where the numerical value has been taken from Table 1 of Ref. 17.

Since the strength of dipole-quadrupole scattering in pressure broadening theory is directly proportional to the quadrupole moment squared, we infer from the numbers given above that the strength of this type of scattering for $H_2O$-$H_2O$ should be roughly 60% of the corresponding strength for $H_2O$-$N_2$. In turn, one knows from pressure broadening calculations that the $H_2O$-$N_2$ dipole-quadrupole strength is typically 20% of the $H_2O$-$H_2O$ dipole-dipole strength. On this simple basis we expect the $H_2O$-$H_2O$ dipole-quadrupole collisions to contribute something like a 10% correction to the broadened halfwidths.

The effect of these collisions will sometimes be enhanced when resonant energy denominators occur in the theory, however, this enhancement cannot be estimated without performing detailed calculations. Preliminary results from our pressure broadening programs indicate that the dipole-quadrupole collisions for $H_2O$-$H_2O$ are negligible at low J, while at high J ($J \gtrsim 12$) they can contribute 10-15% of the total linewidth. This suggests that other mechanisms such as exchange scattering need to be considered.

## 3.0 REFERENCES


1. R. S. Eng, P. L. Kelley, A. Mooradian, A. R. Calawa and T. C. Harman, Chem. Phys. Lett., 19, 524 (1973).

2. R. S. Eng, P. L. Kelley, A. R. Calawa, T. C. Harman and K. W. Nill, Molec. Phys., 28, 653 (1974).

3. R. S. Eng and A. W. Mantz, J. Mol. Spectr. (to be published).

4. P. Cardinet, F. Séverin, A. Valentin, M. Claude and A. Henry, C. R. Acad. Sc. Paris, 284, 37 (1977).

5. P. W. Anderson, Phys. Rev., 76, 647 (1949).

6. C. J. Tsao and B. Curnutte, J. Quant. Spectr. Radiat. Transfer, 2, 41 (1962).

7. R. W. Davies, Phys. Rev., A12, 927 (1975).

8. R. W. Davies and B. A. Oli, J. Quant. Spectr. Radiat. Transfer, 20, 95 (1978).

9. M. Tinkham, Group Theory and Quantum Mechanics (McGraw-Hill, New York, 1964).

10. D. M. Brink and G. R. Satchler, Angular Momentum (Clarendon Press, Oxford, 1968).

11. A. D. Buckingham, Quart. Rev. (London), 13, 183 (1959).

12. G. Birnbaum, Adv. Chem. Phys., 12, 487 (1967).

13. W. S. Benedict and L. D. Kaplan, J. Chem. Phys., 70, 388 (1959).

14. M. W. P. Strandberg, Microwave Spectroscopy (John Wiley and Sons, New York, 1954).

15. H. C. Allen, Jr. and P. C. Cross, Molecular Vib-Rotors (John Wiley and Sons, New York, 1963).

16. Our numerical results indicate that IIR and IIIR should be interchanged in Table 2n2 of Ref. 15.

17. D. E. Stogryn and A. P. Stogryn, Molec. Phys., 11. 371 (1966). In applying the results of the above authors, two points should be noted. First, their labeling of (x, y, z) does not correspond to a IR representation for $H_2O$. Secondly, their tensor $\bar{\bar{\theta}}$ is 3/2 our tensor $\bar{\bar{Q}}^{t}$ as defined in Eq. (1).

18. H. Goldstein, Classical Mechanics (Addison-Wesley, Reading, Mass., 1959), Chapter 4.

# APPENDIX A

## MATRIX ELEMENTS OF $[\phi^2_{z\alpha} - \frac{1}{3}]$

## APPENDIX A

### Matrix Elements of $[\Phi^2_{Z\alpha} - \frac{1}{3}]$

We wish to evaluate Eq. (7) by introducing a complete set

$$\sum_{JKm} |J\ K\ m\rangle \langle J\ K\ m| = 1$$

of symmetric top states. Since J, m are also good quantum numbers for the asymmetric rotor, we obtain

$$\langle J\ \tau\ m|\overset{*t}{Q}_{ZZ}|J'\ \tau'\ m\rangle$$

$$= \sum_{\alpha=x,y,z} Q_{\alpha\alpha} \sum_{KK'} \langle J\ \tau\ m|J\ K\ m\rangle \langle J\ K\ m|[\Phi^2_{Z\alpha} - \tfrac{1}{3}]|J'\ K'\ m\rangle$$

$$\langle J'\ K'\ m|J'\ \tau'\ m\rangle. \qquad \text{(A1)}$$

The symmetric top wave functions have the form[6]

$$\psi_{JKm}(\theta,\psi,\phi) = e^{im\phi}\, e^{iK\psi}\, f_{JKm}(\theta), \qquad \text{(A2)}$$

where $(\theta,\psi,\phi)$ are the three Euler angles.

The direction cosines $(\Phi_{Zx}, \Phi_{Zy}, \Phi_{Zz})$ can be expressed as[18]

$$\Phi_{Zz} = \cos\theta$$

$$\Phi_{Zx} = \sin\theta\sin\psi$$

$$\Phi_{Zy} = \sin\theta\cos\psi \qquad , \qquad \text{(A3)}$$

which are independent of $\phi$. It follows that

$$[\Phi^2_{Zz} - \tfrac{1}{3}] = \tfrac{2}{3}\sqrt{\tfrac{4\pi}{5}}\, Y_{20}(\theta,\psi) \ , \qquad \text{(A4)}$$

$$[\Phi^2_{Zx} - \tfrac{1}{3}] = -\tfrac{1}{3}\sqrt{\tfrac{4\pi}{5}}\, Y_{20}(\theta,\psi)$$

$$-\sqrt{\tfrac{2\pi}{15}}\,(Y_{22}(\theta,\psi) + Y_{2-2}(\theta,\psi))\,, \qquad \text{(A5)}$$

$$[\Phi^2_{Zy} - \tfrac{1}{3}] = -\tfrac{1}{3}\sqrt{\tfrac{4\pi}{5}}\, Y_{20}(\theta,\psi)$$

$$+\sqrt{\tfrac{2\pi}{15}}\,(Y_{22}(\theta,\psi) + Y_{2-2}(\theta,\psi))\,, \qquad \text{(A6)}$$

where the Y's are spherical harmonics with the Condon and Shortley choice of phases.

The matrix element which are needed in Eq. (A1) are readily obtained using the formula[6]

$$\langle J\ K\ m|Y_{jk}(\theta,\psi)|J'\ K'\ m'\rangle$$

$$= (-1)^k\sqrt{\tfrac{2j+1}{4\pi}}\,\sqrt{\tfrac{2J'+1}{2J+1}}\,(J'\ j\ K'\ k|J'\ j\ J(k+K'))\,\delta_{K,k+K'}$$

$$\cdot\,(J'\ j\ m'\ 0|J'\ j\ J\ m')\,\delta_{m,m'}. \qquad \text{(A7)}$$

# A P P E N D I X  B

MATRIX ELEMENTS OF A AND B (EQS. 18-20) FOR $H_2O$ IN A IR REPRESENTATION FOR SOME LOW J QUADRUPOLE TRANSITIONS.

## APPENDIX B

Matrix Elements of A and B (Eqs. 18-20) for $H_2O$ in a IR Representation for Some Low J Quadrupole Transitions. (A and B elements are dimensionless and satisfy the sum rules in Eq. (19); energies are in units $cm^{-1}$.)

| $J, K_a, K_c$ | $J', K'_a, K'_c$ | $E_J$ | $E_J - E_{J'}$ | $\langle J\|A\|J'\rangle$ | $\langle J\|B\|J'\rangle$ |
|---|---|---|---|---|---|
| 0, 0, 0 | 2, 0, 2 | 00.00 | - 70.09 | .99040 | .13822 |
| 0, 0, 0 | 2, 2, 0 | 00.00 | -136.16 | -.13822 | .99040 |
| 1, 0, 1 | 1, 0, 1 | 23.79 | 00.00 | -.63246 | .00000 |
| 1, 0, 1 | 2, 2, 1 | 23.79 | -111.11 | .00000 | -.81650 |
| 1, 0, 1 | 3, 0, 3 | 23.79 | -112.97 | .74391 | .16089 |
| 1, 0, 1 | 3, 2, 1 | 23.79 | -188.36 | -.21586 | .55448 |
| 1, 1, 0 | 1, 1, 0 | 42.37 | 00.00 | .31623 | -.54772 |
| 1, 1, 0 | 2, 1, 2 | 42.37 | - 37.13 | .70711 | .40825 |
| 1, 1, 0 | 3, 1, 2 | 42.37 | -130.99 | .62988 | -.11805 |
| 1, 1, 0 | 3, 3, 0 | 42.37 | -243.05 | -.05704 | .72069 |
| 1, 1, 1 | 1, 1, 1 | 37.14 | 00.00 | .31623 | .54772 |
| 1, 1, 1 | 2, 1, 1 | 37.14 | - 58.04 | .70711 | -.40825 |
| 1, 1, 1 | 3, 1, 3 | 37.14 | -105.14 | .63088 | .23203 |
| 1, 1, 1 | 3, 3, 1 | 37.14 | -248.08 | -.04465 | .69245 |

# A P P E N D I X  C

## PROGRAM LISTING OF QUADRUPOLE MOMENT SUBROUTINES

```
RUN(S,,1011,,,,77777)
ATTACH(SAC,ASMROTUPDATE,ID=CLOUGH,MR=1.
UPDATE(P=SAC,F)
REWIND,COMPILE.
RUN(S,,,COMPILE)
RETURN,SAC,COMPILE.
ATTACH(SAC,QUADM,ID=DAVIES,MR=1.)
RUN(S,,,SAC)
LOSET(PRESET=INDEF)
MAP,PART.
REQUEST,TAPE8,*PF.
LOAD(LGO)
EXECUTE.
EXIT.
```



```
*ID QUADMO
*I ASMROT.1
                        NOLIST
*I ASMROT.18
      COMMON/QUADOF/IFQDEV,IFQDOD
*I ASMROT.46
      READ(INTAPE,921) IFQDEV,IFQDOD
  921 FORMAT(2I5)
*I ASMROT.114
      IF(IFQDEV.EQ.0) CALL QUADEV
      IF(IFQDOD.EQ.0) CALL QUADOD
```

```
      PROGRAM CRLAS (INPUT,OUTPUT,TAPE7,TAPE1,TAPE5=INPUT,TAPE6=OUTPUT,
     1  TAPE2,TAPE8)
      COMMON /XYZ/ INTAPE,LEAVE,JUGGLE,JPUNCH,LSTOR,LOUT,LTAPES(4)
      COMMON/WRTCNT/IWRTCN
      LOUT=6
      JUGGLE=0
      JUGGLE=6
      JUGGLE=1
      LSTOR=0
      LSTOR=7
      LSTOR=6
      LSTOR=2
      CALL FTNBIN(1,0,DUMMY)
   10 CONTINUE
      INTAPE=5
      JPUNCH=1
      LEAVE=1
      LEAVE=6
      CALL ASMROT
      WRITE(6,900) IWRTCN
  900 FORMAT(10X,*IWRITECOUNT=*,I10)
C     CALL LSTSO
      STOP
      END
      SUBROUTINE PHITOP (G,V)
      DIMENSION G(39),V(39)
      COMMON /CONSTID/ OPID(40),SYMID(40)
      DATA (SYMID(I),I=1,39)                    /6H  100 ,6H  0   ,6H  001 ,
     $ 6H  200 ,6H  110 ,6H  020 ,6H  101 ,6H  011 ,6H  0   ,
     $ 6H  300 ,6H  210 ,6H  120 ,6H  030 ,6H  201 ,6H      ,6H  021 ,
     $ 6H  102 ,6H  012 ,6H  003 ,
     $ 6H  040 ,6H  130 ,6H  220 ,6H  310 ,6H  050 ,6H      ,6H  230 ,
     $ 6H  320 ,6H  060 ,6H  150 ,6H  240 ,6H  330 ,6H      ,
     $ 6H  031 ,6H  121 ,6H  211 ,6H  301 ,6H  041 ,6H      ,6H  090 /
      DO 30 J=1,39
```

```
      OPID(J)=SYMID(J)
   30 V(J)=G(J)
      RETURN
      END
      SUBROUTINE QUADEV                                                  000100
C     SUBROUTINES QUADMOMENT                                             000110
C     THESE SUBROUTINES COMPUTE REDUCED MATRIX ELEMENTS OF THE           000120
C     TRACELESS QUADRUPOLE MOMENT OPERATOR FOR ASYMMETRIC ROTOR          000130
C     MOLECULES POSSESSING AN AXIS OF SYMMETRY                           000140
C                                                                        000150
C     THE REDUCED MATRIX ELEMENTS ARE GIVEN BY                           000160
C     (J,TAU//Q//JP,TAUP)=(-1)**(JP-J)*((Q(Z,Z)-Q(X,X)/2-Q(Y,Y)/2)*AWIG 000170
C     -SQRT(3/4)*(Q(X,X)-Q(Y,Y))*BWIG) , WHERE Q(Z,Z),Q(X,X),Q(Y,Y) ARE 000180
C     THE PRINCIPAL AXIS COMPONENTS OF THE PERMANENT QUADRUPOLE MOMENT   000190
C     TENSOR , AND WHERE THE MATRIX ELEMENTS                             000200
C     AWIG=(J,TAU/A/JP,TAUP)                                             000210
C     BWIG=(J,TAU/B/JP,TAUP)                                             000220
C     ARE COMPUTED IN THE SUBROUTINES WHICH FOLLOW .                     000230
C                                                                        000240
C     SUM RULES FOR AWIG,BWIG                                            000250
C     LET A2=AWIG**2 , B2=BWIG**2 , AB=AWIG*BWIG                         000260
C     A2 SUMMED OVER JP,TAUP EQUALS ONE .                                000270
C    A2 MULTIPLIED BY (2*J+1)/(2*JP+1) AND SUMMED OVER J,TAU EQUALS ONE  000280
C     B2 SUMMED OVER JP,TAUP EQUALS ONE                                  000290
C    B2 MULTIPLIED BY (2*J+1)/(2*JP+1) AND SUMMED OVER J,TAU EQUALS ONE  000300
C     AB SUMMED OVER JP,TAUP VANISHES                                    000310
C    AB MULTIPLIED BY (2*J+1)/(2*JP+1) AND SUMMED OVER J,TAU VANISHES    000320
C                                                                        000330
      COMMON /XYZ/ INTAPE,LEAVE,JUGGLE,JPUNCH,LSTOR,LOUT,LTAPES(4)       000340
      COMMON IFEDIG,IFTRPS,IFTRQS,IFTRRW,IFTRQW,IFEXPP,IFPSUM,IFLIST,    000350
     1       IFSTAR,IFCHOY,IFCLOK,IFPUNC,INDSUB(20)                      000360
      COMMON W0,CXX,CYY,CZZ,T1,T2,T3,T4,T5,T6,PHI(30)                    000370
      COMMON    BPC,COREK,BMC,D1,D2,D3,D4,D5,D6,HH(30)                   000380
      COMMON JJ, JMIN, JMAX, JSYM,KDIM(4,2),LSYM(4,2),DEGEN(2), WJMAX    000390
      COMMON NDIM,KP(31,4),KO(31,4),WJHI(31,4),WJLO(31,4),HLAMD(31,4,2),000400
```

```
     2    BOLTZ(31,4,2),MAT1(31,31),MAT2(31,31),MAT3(31,31),MAT4(31,31),000410
     3       TJHI(31,31,4)                                                000420
      COMMON /INT/ ITEMP,TEMP(3),OSUM,BOTLIM,UPLIM,RFREQ,KDIP,            000430
     C             IDIP(3),DIPOLE(3),DPHI(9,3),DIPSQ(3)                  000440
      COMMON /VECLO/ TJLO(31,31,4)                                        000450
      COMMON /XRC/ RC,RELO,SUMINT1,SUMINT2,SUMINT3                        000460
      COMMON /ENDJ/ EJ,P2,P4,P6                                           000470
      COMMON /SELEC/ XDIP,XTYP                                            000480
      COMMON/QUADOF/IFODEV,IFODOD                                         000490
      COMMON/QUAD/ KDIM3(4),LSYM3(4),AQD(31,31),BQD(31,31),WJLOO(31,4),   000500
     1    HLAMD3(31,4),BOLTZ3(31,4),TJLOO(31,31,4)                       000510
      IF(INDSUB(3).NE.0) GO TO 20                                         000520
      INDSUB(3)=1                                                         000530
      CALL FREQQD(0,0,0,0,0)                                              000540
      READ(INTAPE,900) JFREMN,JFREMX,(IDIP(I),I=1,3),BOTLIM,UPLIM,RELOR   000550
  900 FORMAT(2I5,5X,3I5,2F10.3,E10.3)                                     000560
      IF(JFREMN.LE.JMIN) JFREMN=JMIN+1                                    000570
      IF(JFREMX.GT.JMAX) JFREMX=JMAX                                      000580
      IF(LOUT.EQ.JUGGLE) RETURN                                           000590
   20 CONTINUE                                                            000600
      IF(JJ.LT.JFREMN-1) RETURN                                           000610
      IF(JJ.LT.0) RETURN                                                  000620
      IF(JJ.EQ.JMIN) WRITE(LOUT,901) JJ,JMIN,JMAX,JFREMN,JFREMX           000630
  901 FORMAT(10X,*JJ=*,I3,2X,*JMIN=*,I3,2X,*JMAX=*,I3,2X,*JFREMN=*,I3,    000640
     1     2X,*JFREMX=*,I3,2X,*FOR DELTAJ EVEN*)                          000650
C     JJ=0 GIVES NO MATRIX ELEMENTS                                       000660
      IF(JJ.EQ.0)RETURN                                                   000670
      IF(JJ.EQ.JFREMX) IFODEV=1                                           000680
C      QINTNS=QINTNS(L,LP,ITYPE)                                          000690
C     FREQQD=FREQQD(L,LP,ITYPE,INCKPA,INCKPB)  .  THE LA    TWO          000700
C     PARAMETERS IN FREQQD REPRESENT VALUES FOR THE A,B     RICES WHICH  000710
C     ENTER INTO SUBROUTINE CSOM13 IN THE FORM IDEL=(KD     (NCKP)/2 .   000720
C     CAUTION....INCKPA,INCKPB MUST BE EVEN. PRESENT P'     DURE         000730
C     LIMITS TRANSITIONS TO DELTA(KA)=0,2,-2                              000735
C     DO JP=J TRANSITIONS FOR A AND B                                     000740
```

C.4

```
C     IN JP=J CASE , A AND B ARE HERMITIAN , IT IS ONLY NECESSARY TO     000750
C     CALL FREQDD FOR INCKPA AND INCKB VALUES GREATER OR EQUAL ZERO.     000760
      CALL QINTNS(1,1,0)                                                000770
C     DO STRONG (SYMMETRIC TOP) TRANSITIONS .                           000780
      CALL FREQDD(1,1,0,0,2)                                            000790
C     NOW ADD SOME WEAKER TRANSITIONS .                                 000800
      CALL FREQDD(1,1,0,2,0)                                            000810
C     E- DOESNT EXIST FOR JJ LESS THAN OR EQUAL TO ONE .                000830
      IF(JJ.EQ.1) GO TO 85                                              000840
      CALL QINTNS(2,2,0)                                                000850
C     DO STRONG (SYMMETRIC TOP) TRANSITIONS .                           000860
      CALL FREQDD(2,2,0,0,2)                                            000870
C     NOW ADD SOME WEAKER TRANSITIONS .                                 000880
      CALL FREQDD(2,2,0,2,0)                                            000890
   85 CONTINUE                                                          000910
      CALL QINTNS(3,3,0)                                                000920
C     DO STRONG (SYMMETRIC TOP) TRANSITIONS .                           000930
      CALL FREQDD(3,3,0,0,2)                                            000940
      CALL FREQDD(3,3,0,-99,0)                                          000950
C     NOW ADD SOME WEAKER TRANSITIONS .                                 000960
      CALL FREQDD(3,3,0,2,-99)                                          000970
      CALL QINTNS(4,4,0)                                                000980
C     DO STRONG (SYMMETRIC TOP) TRANSITIONS .                           000990
      CALL FREQDD(4,4,0,0,2)                                            001000
      CALL FREQDD(4,4,0,-99,0)                                          001010
C     NOW ADD SOME WEAKER TRANSITIONS .                                 001020
      CALL FREQDD(4,4,0,2,-99)                                          001030
      IF(JJ.LT.JFREQMN+1) GO TO 2000                                    001040
C     DO JP=J-2 TRANSITIONS FOR A,B  .                                  001050
C     SKIP CALCULATION FOR J=1 .                                        001060
      IF(JJ.LE.1) GO TO 2000                                            001070
      CALL QINTNS(1,1,2)                                                001080
C     DO STRONG (SYMMETRIC TOP) TRANSITIONS .                           001090
      CALL FREQDD(1,1,2,0,2)                                            001100
      CALL FREQDD(1,1,2,-99,-2)                                         001110
```

```
C       NOW ADD SOME WEAKER TRANSITIONS .                                  001120
        CALL FREQQD(1,1,2,2,0)                                             001130
        CALL FREQQD(1,1,2,-2,-99)                                          001140
C       E- DOESNT EXIST FOR JP=JJ-2=0                                      001170
        IF(JJ.EQ.2) GO TO 88                                               001180
        CALL QINTNS(2,2,2)                                                 001190
C       DO STRONG (SYMMETRIC TOP) TRANSITIONS .                            001200
        CALL FREQQD(2,2,2,0,2)                                             001210
        CALL FREQQD(2,2,2,-99,-2)                                          001220
C       NOW ADD SOME WEAKER TRANSITIONS .                                  001230
        CALL FREQQD(2,2,2,2,0)                                             001240
        CALL FREQQD(2,2,2,-2,-99)                                          001250
   88 CONTINUE                                                             001280
        CALL QINTNS(3,3,2)                                                 001290
C       DO STRONG (SYMMETRIC TOP) TRANSITIONS .                            001300
        CALL FREQQD(3,3,2,0,2)                                             001310
        CALL FREQQD(3,3,2,-99,-2)                                          001320
        CALL FREQQD(3,3,2,-99,0)                                           001330
C       NOW ADD SOME WEAKER TRANSITIONS .                                  001340
        CALL FREQQD(3,3,2,2,-99)                                           001350
        CALL FREQQD(3,3,2,-2,-99)                                          001360
        CALL QINTNS(4,4,2)                                                 001390
C       DO STRONG (SYMMETRIC TOP) TRANSITIONS .                            001400
        CALL FREQQD(4,4,2,0,2)                                             001410
        CALL FREQQD(4,4,2,-99,-2)                                          001420
        CALL FREQQD(4,4,2,-99,0)                                           001430
C       NOW ADD SOME WEAKER TRANSITIONS .                                  001440
        CALL FREQQD(4,4,2,2,-99)                                           001450
        CALL FREQQD(4,4,2,-2,-99)                                          001460
 2000 CONTINUE                                                             001490
        RETURN                                                             001500
        END                                                                001510
        SUBROUTINE QUADQD                                                  001520
        COMMON /XYZ/ INTAPE,LEAVE,JUGGLE,JPUNCH,LSTOR,LO      TAPES(4)    001530
        COMMON IFEDIG,IFTRPS,IFTROS,IFTRRW,IFTROW,IF   SUM,IFLIST,         001540
```

```
     1        IFSTAR,IFCHOY,IFCLOK,IFPUNC,INDSUB(20)                          001550
      COMMON W0,CXX,CYY,CZZ,T1,T2,T3,T4,T5,T6,PHI(30)                        001560
      COMMON     BPC,COEEK,BMC,D1,D2,D3,D4,D5,D6,HH(30)                      001570
      COMMON JJ, JMIN, JMAX, JSYM,KDIM(4,2),LSYM(4,2),DEGEN(2), WJMAX        001580
      COMMON NDIM,KP(31,4),KO(31,4),WJHI(31,4),WJLO(31,4),HLAMD(31,4,2),     001590
     2    BOLTZ(31,4,2),MAT1(31,31),MAT2(31,31),MAT3(31,31),MAT4(31,31),     001600
     3        TJHI(31,31,4)                                                  001610
      COMMON /INT/ ITEMP,TEMP(3),QSUM,BOTLIM,UPLIM,RFREG,KDIP,               001620
     C             IDIP(3),DIPOLE(3),DPHI(9,3),DIPSQ(3)                     001630
      COMMON/VECLO/TJLO(31,31,4)                                             001635
      COMMON /XRC/ RC,RELO,SUMINT1,SUMINT2,SUMINT3                           001640
      COMMON /FNOD/ EJ,P2,P4,P6                                              001650
      COMMON /SELEC/ XDIP,XTYP                                               001660
      COMMON/QUADOF/IFQDEV,IFQDOD                                            001670
      COMMON/QUAD/ KDIM3(4),LSYM3(4),AOD(31,31),BOD(31,31),WJLOO(31,4),      001680
     1    HLAMD3(31,4),BOLTZ3(31,4),TJLOO(31,31,4)                           001690
      IF(INDSUB(2).NE.0) GO TO 20                                            001700
      INDSUB(2)=1                                                            001710
      CALL FREQQD(0,0,0,0,0)                                                 001720
      READ(INTAPE,900) JFREMN,JFREMX,(IDIP(I),I=1,3),BOTLIM,UPLIM,RELOQ      001730
  900 FORMAT(2I5,5X,3I5,2F10.3,E10.3)                                        001740
      IF(JFREMN.LE.JMIN) JFREMN=JMIN+1                                       001750
      IF(JFREMX.GT.JMAX) JFREMX=JMAX                                         001760
      IF(LOUT.EQ.JUGGLE) RETURN                                              001770
   20 CONTINUE                                                               001780
C     ONLY STORE FOR J=0,DON'T COMPUTE TRANSITIONS.                          001790
      IF(JJ.LT.JFREMN) GO TO 4000                                            001800
      IF(JJ.EQ.JMIN+1) WRITE(LOUT,901) JJ,JMIN,JMAX,JFREMN,JFREMX            001810
  901 FORMAT(10X,*JJ=*,I3,2X,*JMIN=*,I3,2X,*JMAX=*,I3,2X,*JFREMN=*,I3,       001820
     1     2X,*JFREMX=*,I3,2X,*FOR DELTAJ ODD*)                              001830
C     J=1 GIVES NO DELTAJ=ODD TRANSITIONS.IF J=1 ONLY STORE                  001840
      IF(JJ.EQ.JFREMN)GO TO 2000                                             001850
      IF(JJ.EQ.JFREMX) IFQDOD=1                                              001860
C     DO JP=J-1 TRANSITIONS FOR A,B                                          001870
C     E- DOESNT EXIST FOR JP=JJ-1=1                                          001880
```

```
      IF(JJ.LE.2) GO TO 85                                              001890
      CALL QINTNS(1,2,1)                                                001900
C     DO STRONG (SYMMETRIC TOP) TRANSITIONS .                           001910
      CALL FREQQD(1,2,1,0,2)                                            001920
      CALL FREQQD(1,2,1,-99,-2)                                         001930
C     NOW ADD SOME WEAKER TRANSITIONS .                                 001940
      CALL FREQQD(1,2,1,2,0)                                            001950
      CALL FREQQD(1,2,1,-2,-99)                                         001960
   85 CONTINUE                                                          001980
      CALL QINTNS(2,1,1)                                                001990
C     DO STRONG (SYMMETRIC TOP) TRANSITIONS .                           002000
      CALL FREQQD(2,1,1,0,2)                                            002010
      CALL FREQQD(2,1,1,-99,-2)                                         002020
C     NOW ADD SOME WEAKER TRANSITIONS .                                 002030
      CALL FREQQD(2,1,1,2,0)                                            002040
      CALL FREQQD(2,1,1,-2,-99)                                         002050
      CALL QINTNS(3,4,1)                                                002070
C     DO STRONG (SYMMETRIC TOP) TRANSITIONS .                           002080
      CALL FREQQD(3,4,1,0,2)                                            002090
      CALL FREQQD(3,4,1,-99,-2)                                         002100
      CALL FREQQD(3,4,1,-99,0)                                          002110
C     NOW ADD SOME WEAKER TRANSITIONS .                                 002120
      CALL FREQQD(3,4,1,2,-99)                                          002130
      CALL FREQQD(3,4,1,-2,-99)                                         002140
      CALL QINTNS(4,3,1)                                                002150
C     DO STRONG (SYMMETRIC TOP) TRANSITIONS .                           002160
      CALL FREQQD(4,3,1,0,2)                                            002170
      CALL FREQQD(4,3,1,-99,-2)                                         002180
      CALL FREQQD(4,3,1,-99,0)                                          002190
C     NOW ADD SOME WEAKER TRANSITIONS .                                 002200
      CALL FREQQD(4,3,1,2,-99)                                          002210
      CALL FREQQD(4,3,1,-2,-99)                                         002220
 2000 CONTINUE                                                          002240
C     STORE SMALLER J EIGENVECTOR ARRAYS                                002250
      IF(JJ.EQ.JFREMN-1) GO TO 4000                                     002260
```

```
      DO 3100 L=1,4                                                      002270
      IF(LSYM(L,2).NE.0) GO TO 3100                                      002280
      LIM=KDIM(L,2)                                                      002290
      LSYM3(L)=LSYM(L,2)                                                 002300
      KDIM3(L)=KDIM(L,2)                                                 002310
      IF(LIM.LT.1) GO TO 3100                                            002320
      DO 3020 I=1,LIM                                                    002330
      WJLO0(I,L)=WJLO(I,L)                                               002340
      HLAMD3(I,L)=HLAMD(I,L,2)                                           002350
      BOLTZ3(I,L)=BOLTZ(I,L,2)                                           002360
      DO 3010 J=1,LIM                                                    002370
 3010 TJLO0(I,J,L)=TJLO(I,J,L)                                           002380
 3020 CONTINUE                                                           002390
 3100 CONTINUE                                                           002400
 4000 CONTINUE                                                           002410
      DO 2100 L=1,4                                                      002420
      IF(LSYM(L,1).NE.0) GO TO 2100                                      002430
      LIM=KDIM(L,1)                                                      002440
      IF(LIM.LT.1) GO TO 2100                                            002450
      DO 2020 I=1,LIM                                                    002460
      WJLO(I,L)=WJHI(I,L)                                                002470
      HLAMD(I,L,2)=HLAMD(I,L,1)                                          002480
      BOLTZ(I,L,2)=BOLTZ(I,L,1)                                          002490
      DO 2010 J=1,LIM                                                    002500
 2010 TJLO(I,J,L)=TJHI(I,J,L)                                            002510
 2020 CONTINUE                                                           002520
 2100 CONTINUE                                                           002530
      RETURN                                                             002550
      END                                                                002560
      SUBROUTINE FREQDC(L,LP,ITYPE,INCKPA,INCKPB)                        002570
      COMMON /XYZ/ INTAPE,LEAVE,JUGGLE,JPUNCH,LSTOR,LOUT,LTAPES(4)       002580
      COMMON IFEDIG,IFTRRS,IFTROS,IFTRRW,IFTROW,IFEXPP,IFPSUM,IFLIST,    002590
     1       IFSTAR,IFCHOY,IFCLOK,IFPUNC,INDSUB(20)                      002600
      COMMON W0,CXX,CYY,CZZ,T1,T2,T3,T4,T5,T6,PHICON(30)                 002610
      COMMON    BPC,COEEK,BMC,D1,D2,D3,D4,D5,D6,HH(30)                   002620
```

```
      COMMON JJ, JMIN, JMAX, JSYM,KDIM(4,2),LSYM(4,2),DEGEN(2), WJMAX   002630
      COMMON NDIM,KP(31,4),KO(31,4),WJ(31,4,2),          HLAMD(31,4,2),002640
     1    BOLTZ(31,4,2),                                               002650
     2 H(31,31),PHI(31,31),CO(31,31),MAT4(31,29),TENSIT(31),TENS2(31),  002660
     3       TJHI(31,31,4)                                             002670
      COMMON /VECLO/ TJLO(31,31,4)                                     002680
      COMMON /ENOO/ EJ,P2,P4,P6                                        002690
      COMMON /SELEC/ XDIP,XTYP                                         002700
      COMMON /INT/ ITEMP,TEMP(3),QSUM,BOTLIM,UPLIM,RFREQ,KDIP,         002710
     C             IDIF(3),DIPOLE(3),DPHI(9,3),DIPSQ(3)              002720
      COMMON /XPC/ RC,RELO,SUMINT1,SUMINT2,SUMINT3                     002730
      COMMON /SSS/ SQ(200),KPLO(4),KCDEL(4),XX11(4)                    002740
      COMMON/QUAD/ KDIM3(4),LSYM3(4),AQD(31,31),BQD(31,31),WJLOO(31,4), 002750
     1    HLAMD3(31,4),BOLTZ3(31,4),TJLOO(31,31,4)                     002760
      COMMON/WRTCNT/IWRTCN                                             002770
      IF(INDSUB(10).NE.0) GO TO 70                                     002780
      IWRTCN=0                                                         002790
      INDSUB(10)=1                                                     002800
      READ(INTAPE,900) IPN,INTIND                                      002810
  900 FORMAT(2I5)                                                      002820
   70 IF(L.LE.0) RETURN                                                002830
      LO=ITYPE+1                                                       002840
      JP=JJ-ITYPE                                                      002850
      INCA=(KPLO(L)-KPLO(LP)+INCKPA)/2                                 002860
      INCB=(KPLO(L)-KPLO(LP)+INCKPB)/2                                 002870
C     INCA,INCB PLAY THE ROLE OF IDEL IN SUBROUTINE CSQM13             002880
      IF(LO.EQ.3) GO TO 71                                             002890
      IF((LSYM(L,1).NE.0).OR.(LSYM(LP,LO).NE.0)) RETURN                002900
      GO TO 72                                                         002910
   71 IF((LSYM(L,1).NE.0).OR.(LSYM3(LP).NE.0)) RETURN                  002920
   72 CONTINUE                                                         002930
      MINA=1                                                           002940
      MINB=1                                                           002950
      IF(INCA.LT.0) MINA=1-INCA                                        002960
      IF(INCB.LT.0) MINB=1-INCB                                        002970
```

```
      LIM1=KDIM(L,1)                                                    002980
      IF(LO.EQ.3) GO TO 73                                              002990
      LIM2=KDIM(LP,LO)                                                  003000
      GO TO 74                                                          003010
   73 LIM2=KDIM3(LP)                                                    003020
   74 CONTINUE                                                          003030
      MAXA=LIM1                                                         003040
      MAXB=LIM1                                                         003050
      IF(MAXA+INCA.GT.LIM2) MAXA=LIM2-INCA                              003060
      IF(MAXB+INCB.GT.LIM2) MAXB=LIM2-INCB                              003070
      JPKO=JP+KODEL(LP)                                                 003080
      LTAUA=KP(MINA,L)-KO(MINA,L)                                       003090
      LTAUB=KP(MINB,L)-KO(MINB,L)                                       003100
      LLSYMA=((-1)**LTAUA+3)/2                                          003110
      LLSYMB=((-1)**LTAUB+3)/2                                          003120
      RENOA=SQRT(2.*JP+1)/SQRT(2.*JJ+1)                                 003130
      RENOB=RENOA/SQ(2+1)                                               003140
      IATYPE=1000                                                       003150
      IBTYPE=2000                                                       003160
      IF(INCKPA.EQ.-99) GO TO 590                                       003170
      IF(MINA.GT.MAXA) GO TO 590                                        003180
      DO 600 K=MINA,MAXA                                                003190
      KINC=K+INCA                                                       003200
      HHI=WJ(K,L,1)                                                     003210
      IF(LO.EQ.3) GO TO 500                                             003220
      HLO=WJ(KINC,LP,LO)                                                003230
      GO TO 501                                                         003240
  500 HLO=WJLOO(KINC,LP)                                                003250
  501 CONTINUE                                                          003260
C     XLINE IS NOW THE FREQUENCY .                                      003270
      XLINE=HHI-HLO                                                     003280
C     WE COMPARE XLINE WITH THE UPPER AND LOWER LIMITS AND DISCARD      003290
C     IT IF IT DOES NOT PASS THE TESTS .                                003300
      ABSLIN=ABS(XLINE)                                                 003310
      IF((ABSLIN.LT.BOTLIM).OR.(ABSLIN.GT.UPLIM)) GO TO 590             003320
```

```
      KPP=KP(K,L)+INCKPA                                                  003330
      KOP=JPKO-KPP                                                        003340
      IF(KPP.LT.0.OR.KOP.LT.0) GO TO 600                                  003350
      IF(KPP.GT.JP.OR.KOP.GT.JP)GO TO 600                                 003355
      IF(IFLIST.NE.0) RETURN                                              003360
C     OBTAIN A RESULTS FOR JP=J                                           003370
      IF(ITYPE.EQ.0) AWIG=TRANSM(K,KINC,TJHI,AQD,TJHI,L,LIM1,LP,LIM2)     003380
C     OBTAIN A RESULTS FOR JP=J-1                                         003390
      IF(ITYPE.EQ.1) AWIG=TRANSM(K,KINC,TJHI,AQD,TJLO,L,LIM1,LP,LIM2)     003400
C     OBTAIN A RESULTS FOR JP=J-2                                         003410
      IF(ITYPE.EQ.2) AWIG=TRANSM(K,KINC,TJHI,AQD,TJLOO,L,LIM1,LP,LIM2)    003420
      IF(AWIG.EQ.0.0) GO TO 600                                           003430
C     OBTAIN REVERSED MATRIX ELEMENT                                      003440
C     FIRST CHECK THAT REVERSED MATRIX ELEMENT IS NOT A REPEAT .          003450
      IHI=KO(K,L)+1000*KP(K,L)+1000000*JJ                                 003460
      ILO=KOP+1000*KPP+1000000*JP                                         003470
      IF(ILO.EQ.IHI) GO TO 51                                             003480
      AWIGRV=((-1)**ITYPE)*AWIG                                           003490
   51 CONTINUE                                                            003500
      AWIG=RENOA*AWIG                                                     003510
C     SQUARE MATRIX ELEMENTS TO GIVE A MATRIX LINE STRENGTHS .            003520
      AWIG2=AWIG**2                                                       003530
      IF(ILO.EQ.IHI) GO TO 52                                             003540
      AWIGR2=AWIGRV**2                                                    003550
   52 CONTINUE                                                            003560
      WRITE(8) IATYPE,JJ,KP(K,L),KO(K,L),JP,KPP,KOP,XLINE, HI,            003570
     1    AWIG,AWIG2                                                      003580
      WRITE(LEAVE,904) IATYPE,JJ,KP(K,L),KO(K,L),JP,KPP,K  ,XLINE,HHI,    003590
     1    AWIG,AWIG2                                                      003600
      IWRTCN=IWRTCN+1                                                     003610
  904 FORMAT(10X,I5,3X,3I3,4X,3I3,4(2X,E15.5))                            003620
      IF(ILO.EQ.IHI) GO TO 600                                            003630
C     WRITE REVERSED TRANSITION                                           003640
      XLINE=-XLINE                                                        003650
      WRITE(8) IATYPE,JP,KPP,KOP,JJ,KP(K,L),KO(K,L),X     ,HLO,          003660
```

```
     1    AWIGRV,AWIGR2                                                          003670
      WRITE(LEAVE,904) IATYPE,JP,KPP,KOP,JJ,KP(K,L),KO(K,L),XLINE,HLO,         003680
     1     AWIGRV,AWIGR2                                                        003690
      IWRTCN=IWRTCN+1                                                          003700
  600 CONTINUE                                                                 003710
  590 CONTINUE                                                                 003720
      IF(INCKPB.EQ.-99) GO TO 850                                              003730
      IF(MINB.GT.MAXB) RETURN                                                  003740
      DO 800 K=MINB,MAXB                                                       003750
      KINC=K+INCB                                                              003760
      HHI=WJ(K,L,1)                                                            003770
      IF(LO.EQ.3) GO TO 700                                                    003780
      HLO=WJ(KINC,LP,LO)                                                       003790
      GO TO 701                                                                003800
  700 HLO=WJLOO(KINC,LP)                                                       003810
  701 CONTINUE                                                                 003820
C     XLINE IS NOW THE FREQUENCY .                                             003830
      XLINE=HHI-HLO                                                            003840
C     WE COMPARE XLINE WITH THE UPPER AND LOWER LIMITS AND DISCARD             003850
C     IT IF IT DOES NOT PASS THE TESTS .                                       003860
      ABSLIN=ABS(XLINE)                                                        003870
      IF((ABSLIN.LT.BOTLIM).OR.(ABSLIN.GT.UPLIM)) RETURN                       003880
      KPP=KP(K,L)+INCKPB                                                       003890
      KOP=JPKO-KPP                                                             003900
      IF(KPP.LT.0.OR.KOP.LT.0) GO TO 800                                       003910
      IF(KPP.GT.JP.OR.KOP.GT.JP)GO TO 800                                      003915
      IF(IFLIST.NE.0) RETURN                                                   003920
C     OBTAIN B RESULTS FOR JP=J                                                003930
      IF(ITYPE.EQ.0) BWIG=TRANSM(K,KINC,TJHI,800,TJHI,L,LIM1,LP,LIM2)          003940
C     OBTAIN B RESULTS FOR JP=J-1                                              003950
      IF(ITYPE.EQ.1) BWIG=TRANSM(K,KINC,TJHI,800,TJLO,L,LIM1,LP,LIM2)          003960
C     OBTAIN B RESULTS FOR JP=J-2                                              003970
      IF(ITYPE.EQ.2) BWIG=TRANSM(K,KINC,TJHI,800,TJLOO,L,LIM1,LP,LIM2)         003980
      IF(BWIG.EQ.0.0) GO TO 800                                                003990
C     OBTAIN REVERSED MATRIX ELEMENT                                           004000
```

```
C       FIRST CHECK THAT REVERSED MATRIX ELEMENT IS NOT A REPEAT .          004010
        IHI=KO(K,L)+1000*KP(K,L)+1000000*JJ                                 004020
        ILO=KOP+1000*KPP+1000000*JP                                         004030
        IF(ILO.EQ.IHI) GO TO 61                                             004040
        BWIGRV=((-1)**ITYPE)*BWIG/SQ(2+1)                                   004050
     61 CONTINUE                                                            004060
        BWIG=RENOB*BWIG                                                     004070
C       SQUARE MATRIX ELEMENTS TO GIVE B MATRIX LINE STRENGTHS .            004080
        BWIG2=BWIG**2                                                       004090
        IF(ILO.EQ.IHI) GO TO 62                                             004100
        BWIGR2=BWIGRV**2                                                    004110
     62 CONTINUE                                                            004120
        WRITE(8) IBTYPE,JJ,KP(K,L),KO(K,L),JP,KPP,KOP,XLINE,HHI,           004130
       1   BWIG,BWIG2                                                       004140
        WRITE(LEAVE,904) IBTYPE,JJ,KP(K,L),KO(K,L),JP,KPP,KOP,XLINE,HHI,   004150
       1    BWIG,BWIG2                                                     004160
        IWRTCN=IWRTCN+1                                                     004170
        IF(ILO.EQ.IHI) GO TO 800                                            004180
C       WRITE REVERSED TRANSITION                                           004190
        XLINE=-XLINE                                                        004200
        WRITE(8) IBTYPE,JP,KPP,KOP,JJ,KP(K,L),KO(K,L),XLINE,HLO,           004210
       1    BWIGRV,BWIGR2                                                  004220
        WRITE(LEAVE,904) IBTYPE,JP,KPP,KOP,JJ,KP(K,L),KO(K,L),XLINE,HLO,   004230
       1     BWIGRV,BWIGR2                                                 004240
        IWRTCN=IWRTCN+1                                                     004250
    800 CONTINUE                                                            004260
    850 CONTINUE                                                            004270
        RETURN                                                              004280
        END                                                                 004290
        FUNCTION TRANSM(I,J,UA,CO,UB,LA,LIMA,LB,LIMB)                       004300
        DIMENSION UA(31,31,4),CO(31,31),UB(31,31,4)                         004310
        AA=0.                                                               004320
        DO 20 IA=1,LIMA                                                     004330
        BB=0.                                                               004340
        DO 10 IB=1,LIMB                                                     004350
```

```
   10 BB=BB+CO(IA,IB)*UB(IB,J,LB)                                          004360
   20 AA=AA+UA(IA,I,LA)*BB                                                 004370
      TRANSM=AA                                                            004380
      RETURN                                                               004390
      END                                                                  004400
      SUBROUTINE QINTNS(LA,LB,ITYPE)                                       004410
      COMMON /XYZ/ INTAPE,LEAVE,JUGGLE,JPUNCH,LSTOR,LOUT,LTAPES(4)         004420
      COMMON IFEDIG,IFTRQS,IFTRRS,IFTRQW,IFTRRW,IFEXPF,IFFSUM,IFLIST,      004430
     1       IFSTAR,IFCHOY,IFCLOK,IFPUNC,INDSUB(20)                        004440
      COMMON W0,CXX,CYY,CZZ,T1,T2,T3,T4,T5,T6,PHICON(30)                   004450
      COMMON    BPC,COEEK,BMC,D1,D2,D3,D4,D5,D6,HH(30)                     004460
      COMMON JJ, JMIN, JMAX, JSYM,KDIM(4,2),LSYM(4,2),DEGEN(2), WJMAX      004470
      COMMON NDIM,KP(31,4),KO(31,4),WJHI(31,4),WJLO(31,4),HLAMD(31,4,2),   004480
     2    BOLTZ(31,4,2),   H(31,31),PHI(31,31),CO (31,31),MAT4(31,31),    004490
     3       TJHI(31,31,4)                                                 004500
      COMMON /INT/ ITEMP,TEMP(3),QSUM,BOTLIM,UPLIM,RFREQ,KDIP,             004510
     C             IDIP(3),DIPOLE(3),DPHI(9,3),DIPSQ(3)                   004520
      COMMON /SSS/ SQ(200),KPLO(4),KCDEL(4),XX11(4)                        004530
      COMMON/QUAD/ KDIM3(4),LSYM3(4),AQD(31,31),BQD(31,31),WJLOO(31,4),    004540
     1    HLAMD3(31,4),BOLTZ3(31,4),TJLOO(31,31,4)                       004550
      IF(IFLIST.EQ.1) RETURN                                               004560
      LO=ITYPE+1                                                           004570
      IF(LO.EQ.3) GO TO 50                                                 004580
      IF((LSYM(LA,1).NE.0).OR.(LSYM(LB,LO).NE.0)) RETURN                   004590
      LIMB=KDIM(LB,LO)                                                     004600
      GO TO 51                                                             004610
   50 IF((LSYM(LA,1).NE.0).OR.(LSYM3(LB).NE.0)) RETURN                     004620
      LIMB=KDIM3(LB)                                                       004630
   51 LIMA=KDIM(LA,1)                                                      004640
      CALL CSQM13(AQD,BQD,JJ,ITYPE,LA,LIMA,LB,LIMB)                        004650
      RETURN                                                               004660
      END                                                                  004670
      SUBROUTINE CSQM13(A,B,J,ITYPE,L,LIM,L1,LIM1)                         004680
C     SUBROUTINE CSQM13(A,B,J,ITYPE,L,LIM,L1,LIM1)                         004690
C     PROGRAM SETS UP THE WANG TRANSFORMED MATRICES                        004700
```

```
C     AQD(J,K:JF,KP)  , BQD(J,K:JP,KP) FOR USE WITH CALCULATION          004710
C     OF ASYMMETRIC ROTOR QUADRUPOLE MOMENT MATRIX ELEMENTS .            004720
C     THE SYMMETRIC TOP MATRIX ELEMENTS OF AQD, BQD (I.E. BEFORE         004730
C     WANG TRANSFORMATION ) ARE GIVEN BY%                                004740
C     AQD(J,K;JF,KP)=(JP 2 KP 0/JP 2 J KP) FOR K=KP =ZERO OTHERWISE.     004750
C     BQD(J,K:JP,KP)=(JP 2 KP 2/JP 2 J (KP+2)) FOR K=KP+2               004760
C         =(JP 2 KP -2/JP 2 J (KP-2)) FOR K=KP-2                         004770
C         =ZERO OTHERWISE                                                004780
C     THE CLEBSCH-GORDON COEFFS. ARE DEFINED AS IN CONDON-SHORTLY P.77.  004790
C     PARAMETERS IN CALL LIST .                                          004800
C     A,B=WANG TRANSFORMED MATRICES                                      004810
C     J=J IN COMMENTS ABOVE .                                            004820
C     ITYPE=0(JP=J),   1(JP=J-1) ,  2(JP=J-2) .                          004830
C     L,L1=1(E+) ,  2(E-) ,  3(O+) ,  4(O-)                              004840
C     THE COLUMN INDEX OF A,B RUNS OVER L1 TYPE STATES .                 004850
C     THE ROW INDEX OF A,B RUNS OVER L TYPE STATES .                     004860
C     LIM1=WANG ROW DIMENSION ,I.E. THE NUMBER OF COLUMNS .              004870
C      LIM=WANG COLUMN DIMENSION ,I.E. THE NUMBER OF ROWS .              004880
C     L1,LIM1 GO WITH RIGHT HAND EIGENVECTOR ARRAY .                     004890
C     L,LIM GO WITH (TRANSPOSE) OF LEFT HAND EIGENVECTOR ARRAY .         004900
C                                                                        004910
C                                                                        004920
C     IN THE PROGRAM JF TAKES ON VALUES J , J-1 , J-2                    004930
C     THE FOLLOWING TRANSITIONS ARE STRICTLY EXCLUDED .                  004940
C     J=0 .                                                              004950
C     JP NEGATIVE .                                                      004960
C     JP=0 IS ALLOWED ONLY FOR J=2 ,IS UNALLOWED FOR J=1.                004970
C                                                                        004980
C                                                                        004990
C     IN MAIN PROGRAM MULTIPLY A BY FACT1 AND MULTIPLY B   / FACT2       005000
C     TO GIVE SIMPLE SUM RULES .                                         005010
C     FACT1=SQRT(2.*JP+1)/SQRT(2.*J+1) ,FACT2=FACT1/SQR    )             005020
C                                                                        005030
      DIMENSION A(31,31),B(31,31)                                        005040
      COMMON /SSS/ SQ(200),KPLO(4),KODEL(4),XX11 (  )                    005050
```

```
      KP(I,L)=KPLO(L)+2.*(I-1)                                          005060
C     CAUTION...IN THE PROGRAM KP(I,L) PLAYS THE ROLE OF K IN THE       005070
C     COMMENT SECTION .                                                 005080
C     KPLO(1)=0 (E+) ,KPLO(2)=2 (E-) ,KPLO(3)=1 (O+) KPLO(4)=1 (O-)     005090
C     THE ARRAYS ARE INITIALLY SET TO ZERO ,THUS ELEMENTS NOT           005100
C     RESET REMAIN ZERO.                                                005110
      DO 8 I1=1,31                                                      005120
      DO 8 I=1,31                                                       005130
      A(I,I1)=0.0                                                       005140
    8 B(I,I1)=0.0                                                       005150
      IF(J.EQ.0) GO TO 700                                              005160
      KDEL=KPLO(L)-KPLO(L1)                                             005170
      IF(ITYPE.EQ.1) GO TO 300                                          005180
C     DO DELTA(J) EVEN TRANSITIONS , THE SELECTION RULES FOR A,B ARE    005190
C     (O-,O-) , (O+,O+) , (E-,E-) , (E+,E+)                             005200
C     KDEL=0 THROUGHOUT THIS SECTION .                                  005210
      JP=J-2                                                            005220
      IDEL=KDEL/2                                                       005230
      LIMLO=MAX0(1,1-IDEL)                                              005240
      LIMHI=MIN0(LIM,LIM1-IDEL)                                         005250
      IF(LIMHI.LT.LIMLO) GO TO 102                                      005260
      DO 100 I=LIMLO,LIMHI                                              005270
      I1=I+IDEL                                                         005280
      IF(ITYPE.EQ.2) GO TO 101                                          005290
C     DO JP=J TRANSITIONS FOR A MATRIX                                  005300
      SNUM=3.*KP(I,L)**2-J*(J+1)                                        005310
      NA=2*J-1                                                          005320
      NB=J                                                              005330
      NC=J+1                                                            005340
      ND=2*J+3                                                          005350
C     REMEMBER SQ(I+1)=SQRT(I)                                          005360
      DENOM=SQ(NA+1)*SQ(NB+1)*SQ(NC+1)*SQ(ND+1)                         005370
      GO TO 100                                                         005380
C     DO JP=J-2 TRANSITIONS FOR A MATRIX                                005390
  101 IF(JP.LT.0) GO TO 102                                             005400
```

```
      IA=JP-KP(I,L)+2                                                    005410
      IB=JP-KP(I,L)+1                                                    005420
      IC=JP+KP(I,L)+2                                                    005430
      ID=JP+KP(I,L)+1                                                    005440
      SNUM=SQ(3+1)*SQ(IA+1)*SQ(IB+1)*SQ(IC+1)*SQ(ID+1)                   005450
      NA=2*JP+1                                                          005460
      NB=2*JP+2                                                          005470
      NC=2*JP+3                                                          005480
      ND=JP+2                                                            005490
      DENOM=SQ(NA+1)*SQ(NB+1)*SQ(NC+1)*SQ(ND+1)                          005500
  100 A(I,I1)=SNUM/DENOM                                                 005510
  102 CONTINUE                                                           005520
C     OBTAIN B(1,1) MATRIX ELEMENTS                                      005530
      IF(L.EQ.1.OR.L.EQ.2)GO TO 106                                      005540
      IF(ITYPE.EQ.2)GO TO 103                                            005550
C  B(1,1) FOR JP=J                                                       005560
      SNUM=SQ(3+1)*SQ(J+1)*SQ(J+2)*SQ(J+1)*SQ(J+2)                       005570
      NA=2*J-1                                                           005580
      NB=J                                                               005590
      NC=2*J+2                                                           005600
      ND=2*J+3                                                           005610
      DENOM=SQ(NA+1)*SQ(NB+1)*SQ(NC+1)*SQ(ND+1)                          005620
      GO TO 105                                                          005630
C  B(1,1) FOR JP=J-2                                                     005640
103   IF(JP.LT.0) GO TO 106                                              005650
      SNUM=SQ(JP+1)*SQ(JP+2)*SQ(JP+3)*SQ(JP+4)                           005660
      NA=2*JP+1                                                          005670
      NB=2*JP+2                                                          005680
      NC=2*JP+3                                                          005690
      ND=2*JP+4                                                          005700
      DENOM=SQ(NA+1)*SQ(NB+1)*SQ(NC+1)*SQ(ND+1)                          005710
105   B(1,1)=SNUM/DENOM                                                  005720
      IF(L.EQ.4) B(1,1)=-B(1,1)                                          005730
106   CONTINUE                                                           005740
C  OBTAIN REMAINING B(I,I1) MATRIX ELEMENTS                              005750
```

```
C  FIRST DO UPPER SUPERDIAGONAL (K/K+2)                                  005760
      IDEL=(KDEL+2)/2                                                    005770
      LIMLO=MAX0(1,1-IDEL)                                               005780
      LIMHI=MIN0(LIM,LIM1-IDEL)                                          005790
      IF(LIMHI.LT.LIMLO)GO TO 111                                        005800
      DO 110 I=LIMLO,LIMHI                                               005810
      I1=I+IDEL                                                          005820
      IF(ITYPE.EQ.2) GO TO 108                                           005830
C  DO JP=J TRANSITIONS FOR B MATRIX                                       005840
      IA=J-KP(I,L)-1                                                     005850
      IB=J-KP(I,L)                                                       005860
      IC=J+KP(I,L)+1                                                     005870
      ID=J+KP(I,L)+2                                                     005880
      SNUM=SQ(3+1)*SQ(IA+1)*SQ(IB+1)*SQ(IC+1)*SQ(ID+1)                   005890
      NA=2*J-1                                                           005900
      NB=J                                                               005910
      NC=2*J+2                                                           005920
      ND=2*J+3                                                           005930
      DENOM=SQ(NA+1)*SQ(NB+1)*SQ(NC+1)*SQ(ND+1)                          005940
      GO TO 109                                                          005950
C  DO JP=J-2 TRANSITIONS FOR B MATRIX                                     005960
108   IF(JP.LT.0)GO TO 111                                               005970
      IA=JP-KP(I,L)-1                                                    005980
      IB=JP-KP(I,L)                                                      005990
      IC=JP-KP(I,L)+1                                                    006000
      ID=JP-KP(I,L)+2                                                    006010
      SNUM=SQ(IA+1)*SQ(IB+1)*SQ(IC+1)*SQ(ID+1)                           006020
      NA=2*JP+1                                                          006030
      NB=2*JP+2                                                          006040
      NC=2*JP+3                                                          006050
      ND=2*JP+4                                                          006060
      DENOM=SQ(NA+1)*SQ(NB+1)*SQ(NC+1)*SQ(ND+1)                          006070
109   B(I,I1)=SNUM/DENOM                                                 006080
C  INSERT WANG SQRT(2) FACTOR FOR E+                                      006090
110   IF(L.EQ.1.AND.I.EQ.1)B(I,I1)=SQ(2+1)*B(I,I1)                       006100
```

```
111    CONTINUE                                                          006110
C      NOW DO LOWER SUPERDIAGONAL                                        006120
       IDEL=(KDEL-2)/2                                                   006130
       LIMLO=MAX0(1,1-IDEL)                                              006140
       LIMHI=MIN0(LIM,LIM1-IDEL)                                         006150
       IF(LIMHI.LT.LIMLO) GO TO 116                                      006160
       DO 115 I=LIMLO,LIMHI                                              006170
       I1=I+IDEL                                                         006180
       IF(ITYPE.EQ.2) GO TO 112                                          006190
C      DO JP=J TRANSITIONS FOR B MATRIX                                  006200
       IA=J+KP(I,L)-1                                                    006210
       IB=J+KP(I,L)                                                      006220
       IC=J-KP(I,L)+1                                                    006230
       ID=J-KP(I,L)+2                                                    006240
       SNUM=SQ(J+1)*SQ(IA+1)*SQ(IB+1)*SQ(IC+1)*SQ(ID+1)                  006250
       NA=2*J-1                                                          006260
       NB=2*J                                                            006270
       NC=J+1                                                            006280
       ND=2*J+3                                                          006290
       DENOM=SQ(NA+1)*SQ(NB+1)*SQ(NC+1)*SQ(ND+1)                         006300
       GO TO 113                                                         006310
C      DO JP=J-2 TRANSITIONS FOR B MATRIX                                006320
  112  IF(JP.LT.0) GO TO 116                                             006330
       IA=JP+KP(I,L)-1                                                   006340
       IB=JP+KP(I,L)                                                     006350
       IC=JP+KP(I,L)+1                                                   006360
       ID=JP+KP(I,L)+2                                                   006370
       SNUM=SQ(IA+1)*SQ(IB+1)*SQ(IC+1)*SQ(ID+1)                          006380
       NA=2*JP+1                                                         006390
       NB=2*JP+2                                                         006400
       NC=2*JP+3                                                         006410
       ND=2*JP+4                                                         006420
       DENOM=SQ(NA+1)*SQ(NB+1)*SQ(NC+1)*SQ(ND+1)                         006430
  113  B(I,I1)=SNUM/DENOM                                                006440
C      INSERT WANG SQRT(2) FOR E+                                        006450
```

```
  115 IF(L.EQ.1.AND.I1.EQ.1) B(I,I1)=SQ(2*I+1)*B(I,I1)                    006460
  116 CONTINUE                                                            006470
      GO TO 700                                                           006480
C     NOW DO DELTA(J) ODD TRANSITIONS, IN PARTICULAR DO JP=J-1            006490
C     THE SELECTION RULES ARE (O+,O-) , (O-,O+) , (E+,E-) , (E-,E+)       006500
  300 JP=J-1                                                              006510
C     J=1 , JP=0 IS EXCLUDED                                              006520
      IF(JP.LE.0) GO TO 700                                               006530
      IDEL=KDEL/2                                                         006540
      LIMLO=MAXO(1,1-IDEL)                                                006550
      LIMHI=MINO(LIM,LIM1-IDEL)                                           006560
      IF(LIMHI.LT.LIMLO) GO TO 401                                        006570
      DO 400 I=LIMLO,LIMHI                                                006580
      I1=I+IDEL                                                           006590
C     OBTAIN JP=J-1 MATRIX ELEMENTS OF A                                  006600
      IA=JP-KP(I,L)+1                                                     006610
      IB=JP+KP(I,6)+1                                                     006620
      SNUM=KP(I,L)*SQ(2*I+1)*SQ(IA+1)*SQ(IB+1)                            006630
      NA=JP                                                               006640
      NB=2*JP+1                                                           006650
      NC=JP+1                                                             006660
      ND=JP+2                                                             006670
      DENOM=SQ(NA+1)*SQ(NB+1)*SQ(NC+1)*SQ(ND+1)                           006680
      A(I,I1)=SNUM/DENOM                                                  006690
C     CHANGE SIGN                                                         006700
400   A(I,I1)=-A(I,I1)                                                    006710
  401 CONTINUE                                                            006720
C     OBTAIN JP=J-1 MATRIX ELEMENTS OF B                                  006730
C     FIRST OBTAIN B(1,1) MATRIX ELEMENT                                  006740
      IF(L.EQ.1.OR.L.EQ.2) GO TO 406                                      006750
      IA=JP                                                               006760
      IB=JP+1                                                             006770
      IC=JP+2                                                             006780
      ID=JP+1                                                             006790
      SNUM=SQ(IA+1)*SQ(IB+1)*SQ(IC+1)*SQ(ID+1)                            006800
```

```
      NA=JP                                                              006810
      NB=2*JP+1                                                          006820
      NC=JP+1                                                            006830
      ND=2*JP+4                                                          006840
      DENOM=SQ(NA+1)*SQ(NB+1)*SQ(NC+1)*SQ(ND+1)                          006850
      B(1,1)=SNUM/DENOM                                                  006860
      IF(L.EQ.3) B(1,1)=-B(1,1)                                          006870
  406 CONTINUE                                                           006880
C     OBTAIN REMAINING B MATRIX ELEMENTS                                 006890
C     FIRST DO UPPER SUPERDIAGONAL                                       006900
      IDEL=(KDEL+2)/2                                                    006910
      LIMLO=MAXO(1,1-IDEL)                                               006920
      LIMHI=MINO(LIM,LIM1-IDEL)                                          006930
      IF(LIMHI.LT.LIMLO) GO TO 411                                       006940
      DO 410 I=LIMLO,LIMHI                                               006950
      I1=I+IDEL                                                          006960
      IA=JP-KP(I,L)-1                                                    006970
      IB=JP-KP(I,L)                                                      006980
      IC=JP-KP(I,L)+1                                                    006990
      ID=JP+KP(I,L)+2                                                    007000
      SNUM=SQ(IA+1)*SQ(IB+1)*SQ(IC+1)*SQ(ID+1)                           007010
      NA=JP                                                              007020
      NB=2*JP+1                                                          007030
      NC=JP+1                                                            007040
      ND=2*JP+4                                                          007050
      DENOM=SQ(NA+1)*SQ(NB+1)*SQ(NC+1)*SQ(ND+1)                          007060
      B(I,I1)=SNUM/DENOM                                                 007070
C     INSERT WANG SQRT(2) FACTOR                                         007080
      IF(L.EQ.1.AND.I.EQ.1) B(I,I1)=SQ(2+1)*B(I,I1)                      007090
C     CHANGE SIGNS                                                       007100
  410 B(I,I1)=-B(I,I1)                                                   007110
  411 CONTINUE                                                           007120
C     NOW DO LOWER SUPERDIAGONAL                                         007130
      IDEL=(KDEL-2)/2                                                    007140
      LIMLO=MAXO(1,1-IDEL)                                               007150
```

```
      LIMHI=MIN0(LIM,LIM1-IDEL)                                          007160
      IF(LIMHI.LT.LIMLO) GO TO 700                                       007170
      DO 415 I=LIMLO,LIMHI                                               007180
      I1=I+IDEL                                                          007190
      IA=JP+KP(I,L)-1                                                    007200
      IB=JP+KP(I,L)                                                      007210
      IC=JP+KP(I,L)+1                                                    007220
      ID=JP-KP(I,L)+2                                                    007230
      SNUM=-SQ(IA+1)*SQ(IB+1)*SQ(IC+1)*SQ(ID+1)                          007240
      NA=2*JP                                                            007250
      NB=JP+1                                                            007260
      NC=JP+2                                                            007270
      ND=2*JP+1                                                          007280
      DENOM=SQ(NA+1)*SQ(NB+1)*SQ(NC+1)*SQ(ND+1)                          007290
      B(I,I1)=SNUM/DENOM                                                 007300
C     INSERT WANG SQRT(2) FACTOR                                         007310
      IF(L.EQ.2.AND.I.EQ.1) B(I,I1)=SQ(2+1)*B(I,I1)                      007320
C     CHANGE SIGN                                                        007330
  415 B(I,I1)=-B(I,I1)                                                   007340
  700 CONTINUE                                                           007350
      RETURN                                                             007360
      END                                                                007370
```